

Isochoric Heat Capacity Measurements for Metastable Fluids

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Isochoric heat capacity data of six fluids (CO_2 , N_2O_4 , D_2O , C_7H_{16} , $C_{10}H_{22}$, $C_{12}H_{26}$) in the metastable phase including coexistence states will be presented. Measurements were made using a high-temperature, high-pressure, adiabatic, and nearly constant-volume calorimeter. This method allowed measurements of C_V in the one- and two-phase regions including coexistence curves and metastable phases. The construction of the calorimeter enables to control the thermodynamic state of the measuring system with two independent sensors: a resistance thermometer and a semiconductor layer (cuprous oxide) surrounding the calorimetric vessel (integral adiabatic screen). Measurements were carried out at constant volume by the continuous-heating method in the temperature range from the triple point to the liquid-vapor critical point. Measurements near the phase transition points were carried out using cooling (reverse direction, $dT/d\tau < 0$) runs. During cooling runs the system goes from the one-phase state to the two-phase state. For each measured liquid isochore (up to the critical density) we found penetration of the metastable region. The magnitude of the penetration depth varied from 0.02 (for near-critical isochores) up to 3 K (near the triple point) depending on the measured densities. In the moment, when a sample goes out from the metastable state, the temperature of the system jumps and the temperature run changes from $dT/d\tau < 0$ to $dT/d\tau > 0$. The time of the nonequilibrium phase transition from metastable to stable phase is about 0.3-0.4 s. This process can be very clearly read by recording thermograms (T - τ plots) and from the adiabatic sensor. The system goes from a stable state into the metastable state without any features. Our experimental results indicate that the character of the temperature dependence of C_V does not change, when moving along a isochore, upon the intersection of the coexistence curve and transition into the metastable state. This makes it possible to accurately measure the one-phase C_V at the coexistence curve without using the extrapolation technique. This is especially important for near-critical isochores where such extrapolation can lead to large uncertainties when determining the one-phase C_V at saturation. The results of C_V measurements in the metastable phase are compared with values calculated from fundamental equations of state.

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